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*Research paper*

## Research on the Detonation Process of Explosives Containing Sodium Azide

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**Abstract:** The detonation performance of aluminized energetic materials with enriched nitrogen content is examined. Sodium azide ( $\text{NaN}_3$ , SA) was considered as the component to enhance the nitrogen content in explosive mixtures. SA explosives based on hexogen (RDX) as the representative C-H-N-O explosive, and on ammonium nitrate(V) ( $\text{NH}_4\text{NO}_3$ , AN) were investigated. Powdered ( $\text{Al}_p$ ) or flaked ( $\text{Al}_f$ ) aluminum was added as an energetic additive. Detonation of mixtures with added SA revealed highly non-ideal behaviour. Thermodynamic evaluations have been carried out to assess the magnitude of the energy evolved in explosives with added SA, as well as to examine the possible influence of the formation of aluminum nitride ( $\text{AlN}_{(s)}$ ) on the detonation and explosion parameters. The results obtained indicated that, despite the relatively low observed detonation velocities, aluminized RDX/Al/SA and AN/Al/SA mixtures may attain explosion energies of about of 6 MJ/kg and higher. A considerably lower energetic outcome from the formation of  $\text{AlN}_{(s)}$ , in comparison with  $\text{Al}_2\text{O}_{3(s)}$ , was noted.

**Keywords:** sodium azide, detonation performance, aluminized explosives

**Nomenclature:**

- Al<sub>f</sub> Flaked aluminum  
 Al<sub>p</sub> Powdered aluminum  
 AN Ammonium nitrate(V), NH<sub>4</sub>NO<sub>3</sub>  
 RDX Hexogen, C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>O<sub>6</sub>  
 SA Sodium azide, NaN<sub>3</sub>

**1 Introduction**

In practical applications, the explosives have to meet a variety of requirements, concerning the expected course and final parameters of detonation and explosion, chemical composition of products, and others. An important feature of the detonation products is the outcome of species in the gaseous phase, as they are to turn the explosion energy into useful work, *e.g.* driving of shells or rock shattering. On the other hand, the primordial task of any consideration and investigation of explosives is the control and possible improvement of the magnitude of energy evolved during the explosive transformation [1-3].

Gaseous products are the working medium that imparts the energy evolved in an explosion to the material surroundings. With increased nitrogen content, the work-effectiveness of the explosion products may be improved [4, 5]. In the present paper, sodium azide (NaN<sub>3</sub>, SA) was investigated as a possible component in explosive mixtures in order to enhance the amount of detonation products in the gaseous phase. A slightly positive formation energy of NaN<sub>3</sub> ( $\Delta_f H_{\text{NaN}_3}(298.15) = 21.74 \text{ kJ/mol}$ ) brings a neutral contribution to the energetic balance of mixtures that include SA.

Two kinds of explosive mixtures containing SA were examined. In first series of experiments, hexogen (RDX) was used as a representative of the C-H-N-O type of high explosives. In the second series, ammonium nitrate(V) (AN), which is widely applied in industrial explosives, was considered as the base component. The performance of SA in the presence of aluminum powders was investigated. Some prospective transformation parameters of NaN<sub>3</sub> compositions are shown in Table 1.

**Table 1.** Explosion transformation parameters of SA

Reaction pattern	$\Delta Q$ [MJ/kg]	$V$ [m <sup>3</sup> /kg]
$2\text{NaN}_3 + \frac{1}{2}\text{O}_2 \Rightarrow \text{Na}_2\text{O}_{(s)} + 3\text{N}_2$	3.18	0.503
$\text{NaN}_3 + \frac{1}{2}\text{O}_2 + \frac{1}{2}\text{H}_2 \Rightarrow \text{NaOH}_{(g)} + 1.5\text{N}_2$	2.57	0.746

## 2 Experimental

### 2.1 Ingredients and experimental arrangement

Ternary explosive systems consisting of RDX, AN and SA, with aluminum powder added as an energetic agent, were investigated. The physical features of the ingredients employed were as follow:

- crystalline RDX with 9-14  $\mu\text{m}$  grain dimensions,
- sodium azide with grain size 0.06-0.3 mm,
- AN with grain size 0.06-0.3 mm,
- flaked aluminum ( $\text{Al}_f$ ) with a specific surface of 11000  $\text{cm}^2/\text{g}$  ( $\text{Al} - 82.5\%$ ),
- aluminum powder ( $\text{Al}_p$ ) with 0.2-0.3 mm grain dimensions ( $\text{Al} - 99.2\%$ ).

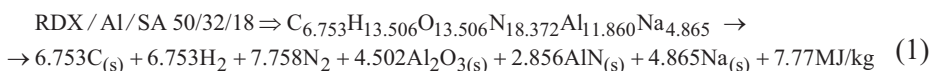
Sample preparation consisted in mechanical mixing of the components added in prescribed proportions. The composition was mixed in a plastic bag until it was seen to be a perfectly homogeneous mass, after about 5 min. Test samples of density 0.9  $\text{g}/\text{cm}^3$  were prepared. Hexogen was purchased from Nitrochem SA (Bydgoszcz, Poland), aluminum powders were provided by Benda Lutz Werke Skawina (Poland), AN was provided by Zakłady Azotowe Puławy (Poland) and SA by Odczynniki Chemiczne (Gliwice, Poland).

Detonation velocity measurements were carried out for charges located in steel or rigid PVC tubes (42 mm outer diameter, 3 mm wall thickness, and 250 mm long). Mean values of the detonation velocity were determined from the records from short-circuit sensors located on three measurement bases 40 mm long.

### 2.2 Investigation of RDX/Al/SA mixtures

An aluminium content of 32% by weight was assumed by investigation of the aluminized mixtures based on RDX. With 32% aluminium content, the maximal energetic outcome may be attained, when all oxygen present in the hexogen participates in reactions with aluminium (to form  $\text{Al}_2\text{O}_3$ ). The heat of explosion then achieves about 10.2 MJ/kg.

When SA was introduced, the RDX/Al/SA composition containing 18% SA (Samples 1 and 2) meets the assumption that all accessible aluminium participates in reactions with oxygen or nitrogen (Equation 1). The maximal energetic outcome is then attained.



Increasing amounts of SA were studied to assess the role and influence

of possible aluminum nitride ( $\text{AlN}_{(s)}$ ) formation in the considered explosive mixtures. The detonation characteristics of the investigated RDX/Al/SA mixtures are presented in Table 2.

**Table 2.** Detonation characteristics of aluminized RDX/Al/SA mixtures

Component	Composition [wt.%]							
	1	2	3	4	5	6	7	8
– RDX	50	50	40	40	30	30	50	30
– Aluminum $\text{Al}_f$	32	–	32	–	32	–	–	–
– Aluminum $\text{Al}_p$	–	32	–	32	–	32	–	–
– SA	18	18	28	28	38	38	50	70
Detonation velocity [m/s] (charge in rigid PVC tube)	2850	2950	2430	2700	1950	2330	3650	2810
$\Delta_f H_{\text{exp}}$ [MJ/kg]	0.199		0.204		0.210		0.306	0.317
$B_T$ [%]	–36.5	–41.2	–35.6	–40.3	–34.6	–39.4	–17.0	–15.1
$N$ [%]	30.6		33.2		35.9		52.2	56.6

Note: “ $N$ ” denotes the percentage of nitrogen (by weight) in the inspected explosives.

### 2.3 Investigation of RDX/Al/AN mixtures

The SA performance in RDX/Al/SA mixtures was studied with compositions in which SA was replaced by AN, in the same concentration ratios. The features and observed detonation velocities for mixtures with AN introduced instead of SA are presented in Table 3.

**Table 3.** Detonation characteristics of RDX/Al/AN mixtures

Component	Composition [wt.%]					
	1	2	3	4	5	6
– RDX	50	50	30	30	50	30
– Aluminum $\text{Al}_f$	32	–	32	–	–	–
– Aluminum $\text{Al}_p$	–	32	–	32	–	–
– AN	18	18	38	38	50	70
Detonation velocity [m/s] (charge in rigid PVC tube)	3180	3450	2860	3050	4480	3900
$\Delta_f H_{\text{exp}}$ [MJ/kg]	–0.683		–1.652		–2.145	–3.113
$B_T$ [%]	–30.7	–35.4	–22.4	–27.1	–0.8	7.5
$N$ [%]	25.2		24.7		36.2	35.9

## 2.4 Investigation of AN/Al/SA mixtures with sodium azide as a dominant component

As AN is a useful and accessible source of oxygen, the performance of SA in mixtures with AN were investigated. The AN/Al/SA mixture containing of 25% of aluminum was chosen as the reference composition. The energetic outcome of the AN/Al/SA 37/25/38 mixture, assuming that all accessible oxygen converts to form  $\text{Al}_2\text{O}_{3(s)}$  (as in Equation 1), is 6.25 MJ/g. A series of experiments was carried out to inspect mixtures in which SA was up to 70 wt.%. The initial characteristics and registered detonation velocities of the considered mixtures are presented in Table 4. The assumed reference state is represented by Sample 2 (AN/Al/SA 37/26/37). The aluminum powder content was increased to 26% to account for the presence of inert coating.

**Table 4.** Sodium azide based AN/Al/SA mixtures

Component	Composition [wt.%]						
	1	2	3	4	5	6	7
– AN	41	37	33	28	18	8	4
– Al <sub>f</sub>	7	7	7	7	7	7	7
– Al <sub>p</sub>	20	19	18	18	18	18	18
– SA	32	37	42	47	57	67	71
Detonation velocity [m/s]							
– steel tube	2630	2470	2420	2380	2180	1950	1720
– rigid PVC tube	2110	2040	1940	–	–	–	–
$\Delta_f H_{\text{exp}}$ [MJ/kg]	-1.76	-1.57	-1.37	-1.12	-0.63	-0.14	0.05
$B_T$ [%]	-18.5	-19.1	-19.6	-21.2	-24.4	-22.7	-29.0
$N$ [%]	35.0	36.9	38.7	40.2	43.1	46.1	47.3

## 3 Analysis

### 3.1 Non-ideality

The investigated explosives are of granular structure, so the detonation process reveals non-ideal behaviour. Three sources of non-ideality may be indicated: combustion of aluminum powder, and reactive transformation of granules of AN and SA. Aluminum behaviour in the detonation wave has been the subject of numerous work *e.g.* [6, 7] and is still the subject of interest [8, 9]. The aluminum particles in the detonation wave undergoes consecutive stages: heating, melting and vaporization (or ablation), and reactions in the gaseous phase. The speed of the

initial stages is considerably lower than that of reactions occurring in the gaseous phase. The lag of energy evolution that occurs by combustion of aluminum particles results in an observed discrepancy between registered and predicted detonation velocities that correspond to full emission of the transformation energy before the C-J surface. Multiphase models are being built to interpret incomplete combustion of aluminum particles before the C-J surface *e.g.* [8, 9]. The equity of pressure and velocity (mechanical equilibrium) is assumed, while thermal non-equilibrium between burning aluminum particles and the reacting medium is considered to attain agreement between the evaluated and experimentally obtained detonation parameters. Also, the inertia of the medium that surrounds the detonation zone has to be accounted for, *e.g.* [9, 10].

The detonation process of AN is known to exhibit substantial dependence of detonation velocity upon charge diameter. The nearly linear critical diameter dependence in the diameter range 15-40 mm for charges of density 1.04 g/cm<sup>3</sup> is quoted in [6]. In a series of experiments carried out in [11], a dependence of the AN detonation velocity on charge diameter up to 303 mm was observed. The critical detonation diameter of hexogen charges, even when hexogen is added up to 70 wt.% by inert material does not exceed a few millimeters [12]. Literature data concerning the reactivity of SA is sparse and the obtained registrations may serve as a reference for further investigations.

In practical applications, *e.g.* in rock blasting, the extension of the working action of the explosive charge into further stages, after the C-J plane (due to afterburning of the internal parts of the energetic grains) is propitious for improving the quality of fragmentation of the loaded rock mass. The recognition of accessible energy in a given energetic mixture is then a task of practical value. In the presented paper thermodynamic calculations were employed to assess the ideal detonation parameters and to estimate the possible energetic outcome of the investigated explosives.

### 3.2 Thermodynamic calculations

In order to assess the detonative transformation of the investigated explosives, thermodynamic evaluations were carried up. The evaluation method, based on the principle of minimization of the thermodynamic potential of the reactive mixture, was applied [13]. The BKW [14] equation of state was used to describe the influence of high temperature and pressure. Illustrative calculations with the developed MWEQ program in which several BKW parameterizations were used are presented in [15]. To assess the interpretation of the investigated explosive mixtures, additional control evaluations were carried out. The results of the control evaluations for hexogen at a density of 0.95 g/cm<sup>3</sup> are presented in Table 5.

**Table 5.** Comparison of evaluation results for RDX at density 0.95 g/cm<sup>3</sup>

BKW parameterization	$D$ [m/s]	$P$ [GPa]	$T$ [K]	$Q_v$ [MJ/kg]	Ref.
BKW Mader	5926.0	9.85	3564	5.779	[14]
BKW Revised	6172.3	10.60	3934	5.824	[16]
BKW H-B	5969.0	10.00	4438	5.927	[17]
BKW H-Bs	6040.6	9.96	4475	5.856	[18]
BKWC	5883.4	8.91	4314	5.570	[19]
Experiment	5800	9.46	–	–	[20]

From the result of that and other control evaluations, the parameterization of BKWC [19] developed from results derived from cylinder test experiments was chosen. In Table 6, the results of control evaluations for ammonium nitrate charges at a density of 0.83 g/cm<sup>3</sup> are compared to the calculations quoted in [11]. In the reported evaluations TIGER, KHT and DTONATE codes were used in which JCZ3 (Jacobs-Cowperthwaite-Zwisler), KHT (Kihara-Nikita-Tanaka) and Cook equations of state were adopted [11].

**Table 6.** Evaluation of detonation properties of AN at density 0.83 g/cm<sup>3</sup>

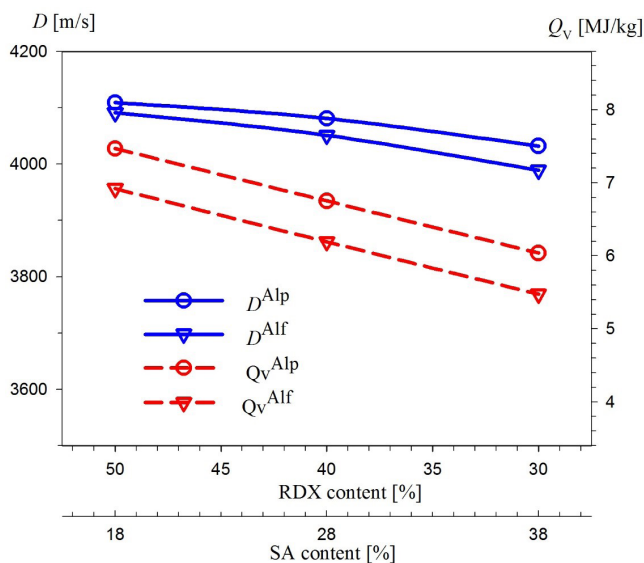
BKW parameterization	$D$ [m/s]	$P$ [GPa]	$T$ [K]	$Q_v$ [MJ/kg]	Ref.
TIGER JCZ3	4.01	3.5	1660	1470	[11]
TIGER BKW	4.71	4.96	1080	1480	
KHT	4.23	3.9	1290	1480	
DTONATE	3.60	2.7	1820	1620	
MWEQ BKWC	3.40	2.8	1693	1580	–

In order to render the non-ideal behaviour of the sodium compounds present in the detonation products, an additional set of BKW covolumes, apart from those given in [19], is necessary. The assumed BKW covolumes were taken as in [21], where they were adjusted in an optimization based on the geometrical concept of Hobbes and Baer [17.]

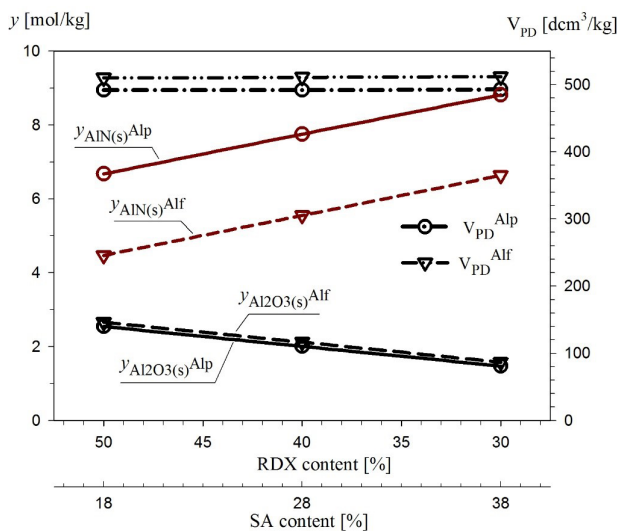
### 3.3 Quantitative analysis

#### 3.3.1 RDX based mixtures of SA

The dependency of the detonation parameters of RDX-based mixtures containing SA on the concentration of SA is presented in Figure 1. The calculations, fulfilling the conditions of thermodynamic equilibrium, confirm the high reactivity of aluminum. The evaluated parameters of the RDX/Al/SA 50/32/18 mixture are listed in Table 7.



(a)



(b)

**Figure 1.** The dependence of detonation parameters of RDX/Al/SA mixtures upon the concentration of SA (aluminum powder ( $\text{Al}_f$  and  $\text{Al}_p$ ) content 32 wt.%): (a)  $D$  – detonation velocity;  $Q_v$  – magnitude of liberated energy; (b)  $V_{PD}$  – volume of detonation products in gaseous phase;  $y_{\text{Al}_2\text{O}_3(\text{s})}$ ,  $y_{\text{AlN}(\text{s})}$  – concentrations of alumina and  $\text{AlN}(\text{s})$



**Table 7.** Evaluation of RDX/Al/SA 50/32/18 mixture

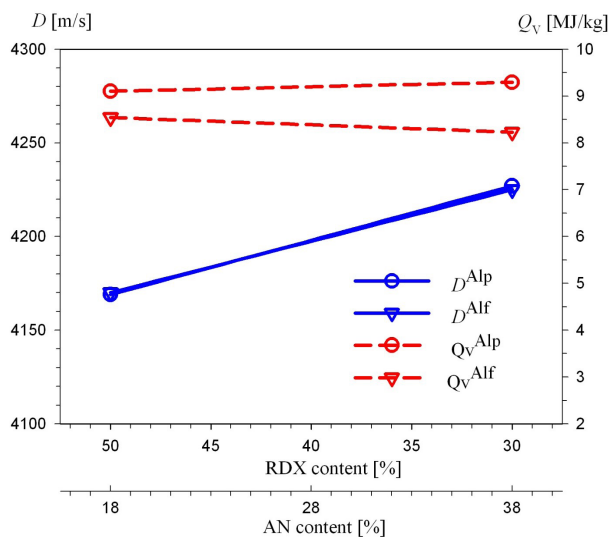
Aluminum type	$D$ [km/s]	$P$ [GPa]	$T$ [K]	$Al_2O_{3(s)}$ [mol/kg]	$AlN_{(s)}$ [mol/kg]	$V_g$ [m <sup>3</sup> /kg]	$Q_v$ [MJ/kg]
– Al <sub>f</sub>	4.09	4.44	4918	2.66	4.46	0.49	6.92
– Al <sub>p</sub>	4.11	4.51	5296	2.55	6.67	0.46	7.48

The obtained magnitude of the detonation energy is quite close to that approximated from Equation 1. The SA present in the mixture acts as the source of nitrogen and improves the energetic balance of the transformation. However, with increasing SA content, an increase of  $AlN_{(s)}$  occurs (Figure 1(b)). In view of the lower formation enthalpy of  $AlN_{(s)}$  in comparison to  $Al_2O_{3(s)}$ , the detonation parameters decrease (Figure 1(a)). Furthermore, the calculated results indicate that the influence of the alumina coating in the case of Al<sub>f</sub> results in a lowering of the detonation parameters in comparison to mixtures containing Al<sub>p</sub>. In the range of SA content considered (18-38%), the aluminum comprised in RDX/SA/Al compositions is able to deliver a reasonable energetic outcome, about 6 MJ/kg.

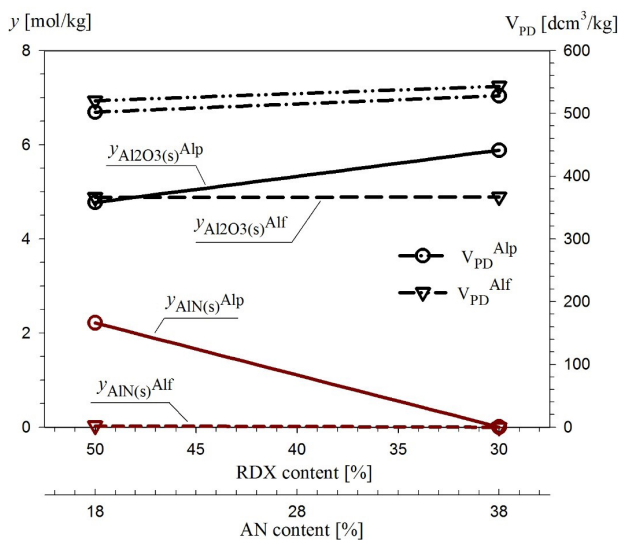
Without an aluminum source (Samples 7 and 8, Table 2), the energetic outcome of RDX/SA mixtures is considerably decreased. The detonation energy obtained in the calculation was 2.88 and 1.92 MJ/kg, respectively. No products in the condensed phase are formed in these cases ( $V_{PD} = 0.96$  m<sup>3</sup>/kg; 0.99 m<sup>3</sup>/kg, respectively). The registered detonation velocities are higher in comparison to compositions containing aluminum powder (3650 and 2810 m/s, respectively).

### 3.3.2 Hexogen-based mixtures with SA replaced by AN

The calculated results obtained for mixtures in which SA was replaced by AN are presented in Figure 2. It may be noted that the introduction of AN, which improves the oxygen balance ( $B_T$ ), leads to a significant increase in detonation energy (Figure 2(a)). Al<sub>p</sub> powder, which possesses a minimal amount of inert coating, valuably improves the transformation parameters in comparison to mixtures with Al<sub>f</sub> added. The volume of explosion products in the gaseous phase is comparable to mixtures containing SA (Figure 1(b)).



(a)

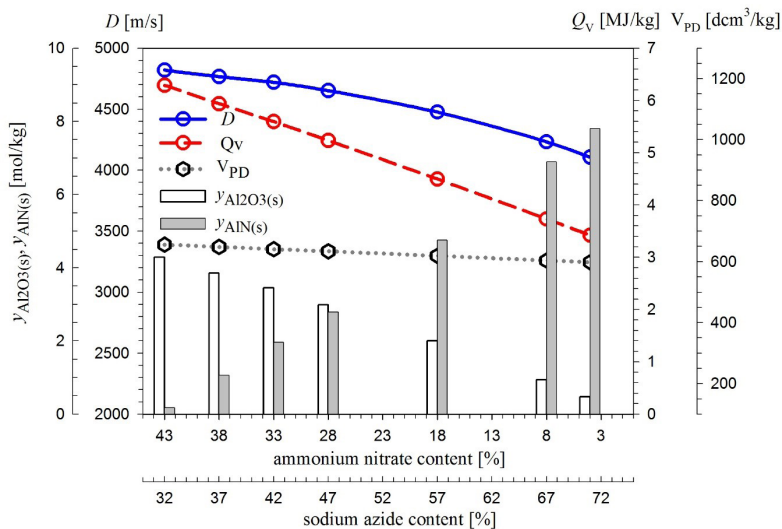


(b)

**Figure 2.** The dependence of detonation parameters of RDX/Al/AN mixtures upon the concentration of hexogen (aluminum powder ( $Al_f$  and  $Al_p$ ) content 32 wt.%): (a)  $D$  – detonation velocity;  $Q_v$  – magnitude of liberated energy; (b)  $V_{PD}$  – volume of detonation products in gaseous phase;  $y_{Al_2O_3(s)}$ ,  $y_{AlN(s)}$  – concentrations of species in condensed phase

### 3.3.3 AN/Al/SA mixtures with sodium azide as a dominant component

The evaluated ideal detonation parameters for the investigated AN/Al/SA mixtures (Table 4) are presented in Figure 3.



**Figure 3.** The dependency of detonation parameters of AN/Al/SA mixtures upon the concentration of SA. Total aluminum powder content 25 wt.%

By calculation, an equal share of aluminum, *i.e.* 7% of  $\text{Al}_f$  and 18% of  $\text{Al}_p$ , was assumed. The increase in SA content results in increasing formation of  $\text{AlN}(\text{s})$ , while the  $\text{Al}_2\text{O}_3(\text{s})$  contribution decreases. The increase in the presence of  $\text{AlN}(\text{s})$  is accompanied by a decrease in the magnitude of the evolved energy. Mixtures containing about 32-42% of SA, quite close to the assumed reference state, are able to deliver about 6 MJ/kg, or even more energy by transformation.

Results for compositions containing of 4 wt.% of AN are reported in [22]. The aluminum powder addition ranged from 2 to 19%, while the SA content ranged from 94 to 77%. The compositions were able to support detonative transformation, but only when placed in steel tubes. The AN/Al/SA 4/2/94 mixture was not able to detonate. The calculated explosion energy ranged from 1 MJ/kg for AN/Al/SA 4/3/93 to about 2.5 MJ/kg for 4/19/77. The SA acts as a source of nitrogen; the volume of gaseous products ranged from 0.9 m<sup>3</sup>/kg to about 0.7 m<sup>3</sup>/kg [22].

## 4 Conclusions

Explosive mixtures of a wide range of content, obtained by addition of sodium azide ( $\text{NaN}_3$ , SA), were investigated. The SA containing explosives were built on two main base components: RDX as a representative of C-H-N-O high explosives, and ammonium nitrate (AN) considered as a representative of industrial explosive mixtures. The energetic output and chemical compositions of the detonation and explosion products were inspected. In view of the excess of nitrogen, caused by the presence of SA, conditions for  $\text{AlN}_{(s)}$  formation were analyzed.

Upon the investigations performed, the following main inferences may be concluded:

- mixtures based on RDX with an SA content of about 20-40 wt.% may deliver about 6 MJ/kg of transformation energy (Table 4 and Figure 1),
- compositions of AN/SA may be considered as an interesting alternative to other explosive mixtures. Mixtures of SA and AN may deliver an explosion energy of 5-6 MJ/kg (Table 4 and Figure 3),
- the energy efficiency of the mixtures considered is due to the presence aluminum powder,
- the considerably lower energetic outcome of  $\text{AlN}_{(s)}$  formation, in comparison to aluminum oxide  $\text{Al}_2\text{O}_{3(s)}$ , should be noted (Figure 3).

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